

cholophæine and biliverdine have shown that they have no apparent relation to hematine, as was formerly supposed, the analyses of uromelanine have made it probable that this substance is a derivative of the coloured part of the blood, cruorine or hematocrystalline, not, however, of hematine, for the atomic weight of hematine is apparently smaller than that of uromelanine. But crystallized cruorine has an atomic weight of about 13,000 ($\text{Fe} = 0.45$ per cent.). From such a body urochrome, including as it does uromelanine, uropittine, omicholine, and perhaps other matters (to be described in future communications), might be derived with an atomic weight of perhaps 1500, being itself near that of albumen (1612), but unable to derive from it. The author thinks it possible that the quantity of blood-disintegration might be measured by determining the amount of uromelanine obtainable from given quantities of urine excreted in given times. In any case uromelanine is one of the most remarkable substances in the whole domain of organic and animal chemistry, and the further study of its metamorphoses cannot fail to yield highly interesting results.

December 19, 1867.

Lieut.-General SABINE, President, in the Chair.

Pursuant to notice given at the last Meeting, Professor Stokes proposed, and Mr. De la Rue seconded, the Right Honourable the Earl of Rosse for election and immediate ballot.

The ballot having been taken, the Earl of Rosse was declared duly elected.

The Bakerian Lecture, "Researches on Vanadium," was delivered by Prof. H. E. Roscoe, Ph.D., F.R.S.

THE BAKERIAN LECTURE.—"Researches on Vanadium."—Part I. By HENRY E. ROSCOE, B.A., F.R.S. Received November 20, 1867.

(Abstract.)

I. Introduction.

Amongst the physical properties which point out the general relationship and classification of chemical compounds, none has so deservedly obtained the confidence of chemists as isomorphism. The vanadium compounds have, however, proved a remarkable and unexplained exception to the conclusions which generally follow from well ascertained identity of crystalline form. Rammelsberg, and afterwards, more completely, Schabus, pointed out the fact that the mineral vanadinite from several localities (a compound of lead vanadate and lead chloride) is isomorphous with apatite, pyromorphite, and mimetesite, minerals consisting of calcium phosphato-chloride, lead phosphato-chloride, and lead arsenato-chloride.

The crystalline form of all these minerals is a hexagonal prism, terminated by 6-sided pyramids. So far indeed has the isomorphism of these

compounds been traced, that in many specimens these minerals have been found to crystallize together in all proportions; and Heddle describes a crystal in his possession, the upper half of which consists of vanadinite and the lower half of pyromorphite.

Our knowledge concerning the chemical composition of the oxides of vanadium is derived from the accurate analytical results of Berzelius, to whose celebrated research (1831) on vanadium we are indebted for almost all we know of this metal and its compounds. From these experiments, more or less completely confirmed by Schafarik and Czudnowicz, it appears that the formula of vanadic acid is VO_3 . Hence it is evident that we have here to do with either a case of dissimilarly constituted substances acting as isomorphous bodies and crystallizing together, or else the conclusions of Berzelius are mistaken, and the true formula of vanadic acid is V_2O_5 , corresponding to phosphorus and arsenic pentoxides. The first of these alternatives has been properly accepted by most chemists as the only present solution of the difficulty, inasmuch as the definite experimental data given by Berzelius render the assumption of any other formula but VO_3 for vanadic acid perfectly gratuitous in the absence of experiments proving these data to be erroneous.

Berzelius based his conclusions on the following experiments, viz. (1) the constant loss of weight which vanadic acid undergoes on reduction in hydrogen at a red heat; (2) the action of chlorine on this reduced oxide, when a volatile chloride is formed and a residue of vanadic acid remains, which is found to be exactly one-third of the quantity originally taken for reduction in hydrogen. Hence Berzelius concludes that the number of atoms of oxygen in the oxide is to that in the acid in the proportion of 1 to 3; so that (assuming the lowest oxide to contain one atom of oxygen) the acid contains three atoms of oxygen, a result which he finds borne out by its capacity of saturation. The question whether the acid contains one or two atoms of metal Berzelius decides in favour of the former view, by finding that no compound corresponding to the alums is formed when vanadic acid is brought together with sulphuric acid and potash. The analyses of the volatile chloride made both by Berzelius and Schafarik confirm this conclusion, and place beyond all doubt the fact that, if the atomic weight of vanadium be taken to be 68.5 and $\text{O}=8$, the formula of vanadic acid is VO_3 , that of the oxide prepared by reduction VO , and that of the chloride VCl_3 .

In the present communication the author, whilst confirming these fundamental results in every particular, still arrives at a totally different conclusion from Berzelius respecting the constitution of vanadic acid and all the other vanadium compounds; for he proves that the true formula of vanadic acid is V_2O_5 , when $\text{O}=16$, and the true atomic weight of vanadium $\text{V}=51.2$, inasmuch as the substance supposed to be vanadium is not the metal but an oxide, with an atomic weight of 67.2, nearly that of Berzelius's metal, whilst the supposed terchloride is an oxychloride.

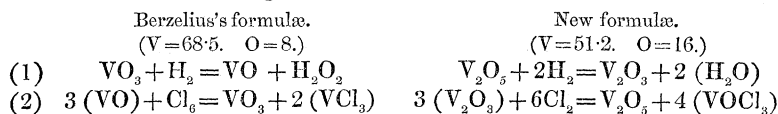
The following are the grounds upon which these conclusions are based; the experimental proofs are contained in the memoir:—

- (1) An oxide of vanadium exists having the atomic weight 67·2 (that of the metal of Berzelius). Hence vanadic acid contains more than three atoms of oxygen.
- (2) The following vanadium oxides have been obtained, both in the dry and wet way, and their composition determined:—

(1) VO*, vanadium monoxide, or vanadyl	= 67·2
(2) V ₂ O ₃ , vanadium sesquioxide (Berzelius's suboxide)	,, 150·4
(3) VO ₂ , vanadium dioxide	,, 83·2
(4) V ₂ O ₅ , vanadium pentoxide (vanadic acid)	,, 182·4
- (3) The so-called terchloride of vanadium, VCl₃ (V = 67·2), contains oxygen; it is an oxychloride having the formula VOCl₃ (V = 51·2); it may be called vanadyl trichloride, or vanadium oxytrichloride, and corresponds to POCl₃, phosphoryl trichloride.
- (4) Three other solid oxychlorides exist, having the composition

(1st) VOCl ₂ , vanadyl dichloride, or vanadium oxydichloride.
(2nd) VOCl, vanadyl monochloride, or vanadium oxymonochloride.
(3rd) V ₂ O ₂ Cl, divanadyl monochloride.
- (5) All the native vanadates are tribasic.
- (6) Vanadium pentoxide fused with sodium carbonate displaces three molecules of carbon dioxide, showing that normal or ortho-sodium vanadate is tribasic, the formula of this salt being Na₃VO₄.
- (7) The so-called monovanadates are salts corresponding to the monobasic phosphates, and may be termed metavanadates; thus, NaVO₃, NH₄VO₃, Ba₂VO₃. The so-called bivanadates are anhydro-salts, similar in constitution to the anhydro-salts of chromic and boric acids.
- (8) Vanadium nitride has been prepared, which, on analysis, was shown to contain 51·2 parts by weight of vanadium to 14 parts of nitrogen.

All the reactions according to which vanadic acid was supposed (Berzelius, Rammelsberg, Schafarik) to contain three atoms of oxygen with an atomic weight V = 67·2, can equally well be explained when V₂O₅ (V = 51·2) is taken to represent the composition of this substance. That this is the case is seen from the following:—



* It is possible that the molecular formulæ of these substances (VO₁VO₂), as well as those of the solid oxychlorides, may be a multiple of the above. Further experiment must decide whether or not these oxides, like the corresponding nitrogen compounds, are an exception to the law of even atomicities.

II. *Occurrence and Preparation of the Vanadium Compounds.*

The sources of vanadium have hitherto yielded the compounds of this metal in extremely small quantities, and consequently our knowledge of the substance is but limited. The attention of the author was drawn to the occurrence of vanadium in some of the copper-bearing beds of the Lower Keuper Sandstone of the Trias, worked at Alderley Edge and Mottram St. Andrews, in Cheshire. He obtained a large quantity of a lime precipitate, containing nearly 2 per cent. of vanadium, obtained in working up a poor cobalt-ore from Mottram in a mine now closed. The precipitate, containing mainly arsenic, iron, lead, copper, vanadium, and lime, with sulphuric and phosphoric acids, was first well furnaced with ground coal, to drive off the greater portion of the arsenic, and then roasted with one-quarter of its weight of soda-ash, so as to convert the vanadium into a soluble vanadate, and on lixiviation arsenic and the heavy metals were completely thrown down by sulphuretted hydrogen. The deep-blue solution was neutralized by ammonia, the precipitated vanadium oxide dried and oxidized by nitric acid, and the crude vanadium pentoxide thus obtained boiled out with a saturated solution of ammonium carbonate. The slightly soluble ammonium vanadate was washed and recrystallized. In order to prepare pure vanadium pentoxide from this salt it was roasted, and the powder thus obtained suspended in water into which ammonia gas was passed. The dissolved ammonium vanadate was separated by filtration from a residue containing silica, phosphates, &c. The pentoxide obtained by heating this salt was free from phosphorus. A second method of preparing the pure vanadium pentoxide consists in decomposing the pure oxychloride in water, and freeing the pentoxide from any traces of silica by exposure to hydrofluoric-acid gas. Great difficulty was experienced in obtaining vanadium free from phosphorus; all the native vanadates contain large quantities of phosphorus. The action of traces of this substance upon vanadium pentoxide is remarkable; 1 per cent. of phosphoric acid renders crystalline vanadium pentoxide black and amorphous, whilst the presence of the merest trace altogether prevents the reduction of the pentoxide in hydrogen.

III. *Atomic Weight determination of Vanadium by reduction of Vanadium Pentoxide in Hydrogen.*

This method was the one originally employed by Berzelius. It is perfectly reliable, and yields accurate results when carried out with care and due regard to the necessary precautions, which are detailed in the memoir.

In drying the pure hydrogen gas only sulphuric acid can be used, as phosphorus pentoxide used in the last drying-tube was found invariably to be carried over into the boat containing the substance; and the presence of a trace of phosphoric acid renders the complete reduction to sesquioxide impossible.

The formula of vanadium pentoxide being V_2O_5 , and that of the oxide obtained by reduction being V_2O_3 , the atomic weight of the metal is found from the equation

$$x = \frac{8(5b-3a)}{a-b}$$

where a = the weight of vanadium pentoxide taken, and
 b = " " sesquioxide obtained.

In each of the determinations a weight of not less than 5 grammes of substance was operated on.

Nos.	Weight of vanadium pentoxide taken.	Weight of vanadium sesquioxide obtained.	Atomic weight of vanadium.
1	7.7397	6.3827	51.26
2	6.5819	5.4296	51.39
3	5.1895	4.2819	51.48
4	5.0450	4.1614	51.35

Hence the mean atomic weight from these experiments is 51.37, with a mean error of ± 0.066 . Berzelius's number, calculated according to the above equation, is 52.55. The difference is probably owing to the fact that his vanadium contained a trace of phosphorus, which prevented the complete reduction.

IV. The Vanadium Oxides.

- (1) Vanadium monoxide, or vanadyl..... VO or V_2O_2
- (2) " sesquioxide (Berzelius's suboxide).. V_2O_3 or $V_2O_2 + O$
- (3) " dioxide (Berzelius's vanadic oxide).. VO_2 or $V_2O_2 + O_2$
- (4) " pentoxide (vanadic acid)..... V_2O_5 or $V_2O_2 + O_3$

(1) *Vanadium Monoxide*, $VO=67.2$.—In its power of uniting with oxygen vanadium surpasses uranium, as observed by Peligot; and as this oxide is found to enter into many of its compounds, the name Vanadyl may appropriately be given to it.

Vanadium monoxide is a grey powder possessing a metallic lustre, and is obtained by passing the vapour of vanadyl trichloride, mixed with excess of hydrogen, through a combustion-tube containing red-hot carbon.

This oxide may be prepared in solution by the action of nascent hydrogen, evolved by metallic zinc, cadmium, or sodium amalgam, upon a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid attains a permanent lavender tint, and contains the vanadium in solution as monoxide. This compound absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring-matters as quickly as chlorine, and far more powerfully than any other known reducing agent. The degree of oxidation of the dissolved vanadium was estimated by a standard solution of permanganate, which had been

proved to give accurate results with a vanadium oxide of known composition, the point of maximum oxidation being obtained when the solution became pink. According to this method, 100 parts of vanadium pentoxide were shown to have lost 26·53 per cent. of oxygen on reduction with zinc; the percentage loss from V_2O_5 to V_2O_3 is 26·3.

When the neutral lavender-coloured solution of a monoxide salt is allowed to stand exposed to the air for a few seconds, the colour changes to a deep chocolate-brown from absorption of oxygen; indeed this reaction for oxygen is as delicate as that of an alkaline pyrogallate. If air be passed through the acid lavender-coloured solution of vanadous sulphate, oxygen is absorbed, and the liquid assumes a permanent blue colour, and the vanadium is contained in solution as dioxide. If the free acid contained in the lavender solution be neutralized by zinc, the liquid on exposure to air attains a permanent brown tint, which, on addition of acids, becomes green, and the solution contains sesquioxide.

(2) *Vanadium Sesquioxide*, $V_2O_3 = 150\cdot4$ (Berzelius's suboxide).—Obtained as a black powder by reducing vanadium pentoxide in hydrogen at red heat. When exposed warm to the air it glows, absorbs oxygen, and passes into the highest oxide. At the ordinary atmospheric temperature it slowly absorbs oxygen, and is converted into dioxide. Vanadium sesquioxide is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen evolved from metallic magnesium upon a solution of vanadic acid in sulphuric acid. The changes of colour observed in the case of the monoxide solutions do not continue beyond the green, and the liquid contains vanadium in solution as sesquioxide. 100 parts of vanadium pentoxide were found to lose, on reduction with magnesium, 17·7 per cent. of oxygen; the loss on reduction to V_2O_3 is 17·5 per cent. Solutions of vanadium sesquioxide can also be obtained by partial oxidation of the lavender-coloured solution containing monoxide.

Chlorine attacks the sesquioxide in the manner first pointed out by Berzelius according to the formula $3(V_2O_3) + 6Cl_2 = V_2O_5 + 4(VOCl_3)$.

(3) *Vanadium Dioxide*, $VO_2 = 83\cdot2$ (the vanadic oxide of Berzelius).—This oxide was obtained by Berzelius by precipitation from its salts. It may also be prepared in the form of blue shining crystals by allowing the sesquioxide to absorb oxygen at ordinary temperatures. It is contained in solutions, having a bright blue colour, prepared by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen, oxalic acid, &c., upon vanadic acid in solution. 100 parts of vanadium pentoxide were found to lose, on reduction with the two first-named agents, 9·03 per cent.; the loss on reduction to VO_2 is 8·75. Solutions containing the dioxide are obtained by passing air through acid solutions of the monoxide until a permanent blue colour is attained.

(4) *Vanadium Pentoxide*, V_2O_5 (vanadic acid = 182·4).—The properties of this oxide and its compounds are considered only so far as is necessary for the elucidation of the true atomic weight of the metal.

Constitution of the so-called Monovanadates.—The analyses of Berzelius serve to point out, when the new atomic weight is adopted, that these compounds prove to be metavanadates; thus—

Berzelius's formulæ.

(V=68·5. O=8.)

Ammonia salt $\text{NH}_3\text{VO}_3 + \text{HO}$
Barium ,, ... BaOVO_3

New formulæ.

(V=51·2. O=16. Ba=137.)

Ammonium metavanadate NH_4VO_3 or $\left. \begin{smallmatrix} \text{NH} \\ \text{VO} \end{smallmatrix} \right\}^4 \text{O}_2$

Barium metavanadate BaV_2O_6 or $\left. \begin{smallmatrix} \text{Ba} \\ 2\text{VO} \end{smallmatrix} \right\} \text{O}_4$

The bivanadates are anhydro-salts having the composition $2(\text{NaVO})_3 + \text{V}_2\text{O}_5$, or perhaps $\text{Na}_4\text{V}_2\text{O}_7 + 3\text{V}_2\text{O}_5$.

Berzelius's analysis of this ammonium salt was carefully confirmed, experiment showing that the salt yielded 77·75 per cent. of vanadium pentoxide, theory requiring 77·82 per cent. The bivanadates analyzed by Von Hauer prove to be anhydro-salts, analogous to certain chromates and borates, and possessing the composition $2(\text{NaVO}_3) + \text{V}_2\text{O}_5$.

The normal or ortho-vanadates are tribasic; the sodium salt is Na_3VO_4 , or $\left. \begin{smallmatrix} \text{Na}_3 \\ \text{VO} \end{smallmatrix} \right\} \text{O}_3$; this is shown by the fact that vanadium pentoxide (V_2O_5), when fused with sodium carbonate, displaces 3 molecules of carbon dioxide.

It is the author's intention to investigate the composition of the vanadates at a future time.

V. Vanadium Oxychlorides, and Second Atomic Weight determination of the Metal.

(1) *Vanadium Oxytrichloride, or Vanadyl Trichloride*, VOCl_3 .—Molecular weight 173·2. The fact that the lemon-coloured liquid chloride of vanadium prepared by the action of chlorine upon the sesquioxide (Berzelius) contains oxygen, contrary to the statements of previous experimenters, was ascertained (1) by obtaining carbon dioxide from the decomposition of the vapour of the oxychloride passing over red-hot charcoal, (2) by the production of magnesia by the action of magnesium, (3) by the formation of caustic soda by the action of sodium, (4) by the formation of vanadium sesquioxide when the vapour of the oxychloride was passed with pure hydrogen through a heated tube.

The specific gravity of vanadyl trichloride was found to be 1·841 at 14°C ., and its vapour-density 88·2 ($\text{H}=1$), or 6·108 ($\text{air}=1$), and its boiling-point $126\cdot7$ under 767·0 millims. (determined on 100 grammes of substance). Vanadyl trichloride, most carefully purified, was analyzed many times with every precaution, the chlorine being estimated both by Gay-Lussac's pro-

cess and by ordinary weight analysis. Nine volumetric analyses gave 61·306 per cent. of chlorine; seven gravimetric determinations gave 61·241 per cent. From these numbers an atomic weight of 51·05 for vanadium is obtained. The mean of 51·05 and 51·37, the number which the reduction experiments yielded, viz. 51·21, is taken as the true atomic weight of vanadium.

The vanadium in this chloride was determined as pentoxide. The result of the analyses is as follows:—

	Calculated.	Found.
V = 51·2	29·55	29·58
Cl ₃ = 106·11	61·24	61·27
O = 16·0	9·21	—
	173·31	100·00

(2) *Vanadium Oxydichloride, or Vanadyl Dichloride*, $\text{VOCl}_2 = 137·9$.—This substance is a light green crystalline solid body, obtained by the action of zinc on the trichloride at 400° in sealed tubes. It has a specific gravity of 2·88, is insoluble in water, but deliquesces on long exposure to air, and dissolves easily in acids. Analysis gave

	Calculated.	Found.
V	37·13	37·58
Cl ₂	51·27	50·73
O	11·60	—
	100·00	

(3) *Vanadium Oxymonochloride, or Vanadyl Monochloride*, $\text{VOCl} = 102·57$. This body is a brown, light, powdery solid, formed by the action of hydrogen upon vanadyl trichloride at a red heat. It is insoluble in water, but readily soluble in acids. Analysis gave

	Calculated.	Found.
V	49·96	50·21
Cl	34·45	34·53
O	15·59	—
	100·00	

(4) *Divanadyl Monochloride*, $\text{V}_2\text{O}_2\text{Cl} = 169·8$. This oxychloride is also formed by the action of hydrogen at a red heat on VOCl_3 . It can readily be separated from the foregoing compound, as it is a heavy, shining, metallic powder, resembling “mosaic gold” in its appearance. Analysis gave

	Calculated.	Found.
V ₂	60·37	61·69
Cl	18·82	18·93
O ₂	20·81	—
	100·00	

VI. *Vanadium Nitrides*.

(1) *Vanadium Mononitride*, $\text{VN}=65\cdot2$.—A greyish powder unalterable in the air, obtained by heating the ammonium oxychloride to whiteness in a current of ammonia. Both vanadium and nitrogen were directly estimated, with the following results:—

	Calculated.	Found.
Vanadium	78·6	77·8
Nitrogen	21·4	20·2

(2) *Vanadium Dinitride*, $\text{VN}_2=79\cdot2$.—A black powder obtained by Uhrlaub on heating the ammonium oxychloride to a moderate temperature. The vanadium was estimated by Uhrlaub, but he did not understand the constitution of the substance, as he assumed the atomic weight of the metal to be 68·5, and did not estimate the nitrogen.

The vanadium nitrides not only demonstrate with absolute certainty the true atomic weight of the metal, but they also serve as the starting-point from which to commence the study of the metal itself, as well as an entirely new class of bodies, viz. the compounds of vanadium with chlorine and the other halogens.

The author hopes to describe these interesting substances in the next communication.

The Society then adjourned over the Christmas Recess to Thursday, January 9th.